

MoP 催化剂上乙炔选择性催化加氢

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摘要: 通过高温还原法制得磷化钼(MoP)催化剂, 采用 X 射线衍射和原位 X 射线光电子能谱对其进行了表征, 并考察其催化乙炔选择性加氢性能. 结果表明, 在 650 °C 经 H₂ 还原制得的催化剂中形成了大量的低价态物种 MoP, 但仍含有大量的高价态 Mo 和 P 物种, 该催化剂具有加氢活性中心和缺电子中心双重功能, 在乙炔选择性加氢反应中, 乙炔转化率超过 99% 时, 乙烯选择性仍能保持在 73% 以上.

关键词: 磷化钼; 乙炔; 选择性加氢; 乙烯

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Selective Hydrogenation of Acetylene over a MoP Catalyst

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Abstract: A MoP catalyst was prepared by high temperature hydrogen reduction. Its properties were investigated by X-ray diffraction and in-situ X-ray photoelectron spectroscopy. It was used for the selective catalytic hydrogenation of acetylene. The results indicated that MoP is formed by hydrogen reduction at 650 °C. The prepared MoP catalyst contained high valence molybdenum and phosphorus species. The catalyst is a bifunctional catalyst, which includes a hydrogenation center and an electron-deficient center. Ethylene selectivity can exceed 73% when the acetylene conversion is higher than 99%.

Key words: molybdenum phosphide; acetylene; selective hydrogenation; ethylene

乙烯可通过高级烷烃热裂解的方法制得, 但其中含有的少量乙炔 (<2%) 对乙烯聚合催化剂具有很强的毒害作用. Pd 催化剂和改性的 Pd 催化剂广泛用于乙炔选择性加氢反应, 而乙炔加氢反应是一个典型的串联反应 ($C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$), 随着乙炔转化率的增加, 乙烯选择性会急剧降低^[1-3]. 未改性的 Pd 催化剂具有非常高的痕量乙炔去除活性, 但乙烯选择性同样很低. 除此之外人们也对其它类型催化剂进行了研究^[4-6]. 但仍主要集中于贵金属催化剂, 对非贵金属催化剂的研究很少. MoP 作为一种新型的加氢催化剂, 引起了人们的广泛关注, 它在加氢脱硫

(HDS) 和加氢脱氮 (HDN) 反应中表现出优越的加氢性能^[7-9]. 但尚未见将 MoP 催化剂用于乙炔催化加氢中的报道.

本文采用高温还原法制得 MoP 催化剂, 并用于乙炔选择性催化加氢制乙烯反应中. 按 Mo/P 摩尔比为 1.0 称取适量的钼酸铵和磷酸氢二铵充分溶于蒸馏水中, 搅拌下于 80 °C 蒸干水分, 在 100 °C 干燥 24 h, 500 °C 焙烧 4 h, 制得钼磷酸盐前驱体, 将其研磨筛分 20~40 目的颗粒. 将制得的前驱体置于石英管反应器中, 在 H₂ 气氛中以 10 °C/min 由室温升到 300 °C, 再以 2 °C/min 由 300 °C 升到 650 °C 并恒温 2 h. 还原

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结束后,在 H_2 气氛中自然冷却到室温,然后用 1% O_2 -99% N_2 混合气进行钝化 6~8 h 以待用。

所制得催化剂的物相在 Rigaku D/Max-2500/PC 型 X 射线衍射 (XRD) 仪上进行测定, $\text{Cu K}\alpha$ 为射线源。原位 X 射线光电子能谱 (in-situ XPS) 测试在 VG ESCALAB MK2 型 X 射线光电子能谱仪上进行。使用 $\text{Al K}\alpha$ 线 ($h\nu = 1486.6 \text{ eV}$), 管电流 20 mA, 管电压 12 kV。电子结合能以 $\text{C } 1s = 285.0 \text{ eV}$ 校正。将样品在 500°C 用 H_2 还原 60 min, 待样品室降至室温后, 抽真空为 $2 \times 10^{-8} \text{ Pa}$, 然后对样品进行 XPS 测试。

乙炔加氢反应在常压于石英管固定床反应器中进行。称取 100 mg MoP 样品装填于反应管中, 于 600°C 用 90 ml/min 高纯 H_2 预处理 60 min, 冷却到设定温度后, 切换通入乙炔和 H_2 含量分别为 1% 和 10% 的混合气, Ar 为平衡气, 由质量控制仪控制气体流量为 60 ml/min。原料和加氢产物通过带有 FID 检测器的气相色谱 (Agilent 6890N) 在线分析, 组分由 GS-GASPRO 型毛细管柱 ($30 \text{ m} \times 0.320 \text{ mm}$) 分离。

图 1 为所制得 MoP 催化剂的 XRD 谱。由图可见, 样品在 27.94° , 32.08° , 43.06° , 57.16° , 57.74° , 64.78° , 67.06° , 67.58° 和 74.12° 处出现明显的衍射峰, 分别对应于 MoP(001), (100), (101), (110), (111), (102) 和 (201) 晶面。未检测到其它物相。由此表明, 钼磷酸盐在 650°C 经 H_2 还原可制得 MoP 物相。

在 H_2 中于 500°C 还原 60 min 的 MoP 催化剂的原位 XPS 谱见图 2。由图可见, 样品在电子结合能为 228.0, 229.1 和 232.2 eV 处出现 Mo $3d_{5/2}$ XPS

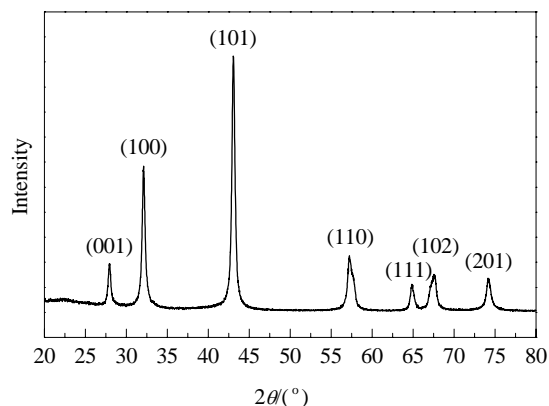


图 1 MoP 催化剂的 XRD 谱

Fig. 1. XRD pattern of the MoP catalyst.

峰, 分别对应于 Mo^{3+} , Mo^{4+} 和 Mo^{6+} 物种; 在电子结合能为 129.2 和 133.4 eV 处形成了与 P^{3-} 和 P^{5-} 物种相对应的 P $2p_{3/2}$ XPS 峰, 与文献结果一致^[10,11]。根据峰面积可得, MoP 表面 P^{3-}/P 和 Mo^{3+}/Mo 比分别为 0.22 和 0.24。由此可知, 通过 H_2 还原在催化剂表面形成了大量的低价态 Mo^{3+} 和 P^{3-} 物种 (MoP), 这与 XRD 结果一致。同时, 该催化剂中仍含有大量的高价态 Mo 和 P 化合物, 这些高价态物种的存在可能会对催化剂活性产生影响。

在 $\text{H}_2/\text{C}_2\text{H}_2 = 10$, 空速为 36000 ml/(g·h), 常压和不同反应温度条件下, 考察了 MoP 催化剂上乙炔加氢反应性能, 结果见图 3。由图可见, 所制得的 MoP 催化剂具有高的乙炔加氢活性, 在 180°C 反应时, 乙炔转化率达 45.2%, 乙烯选择性可达 77.3%, 且两者受反应温度的影响很大, 在 240°C 反应时, 乙炔转化率达 99.5%, 乙烯选择性保持在 73.4% 左右。

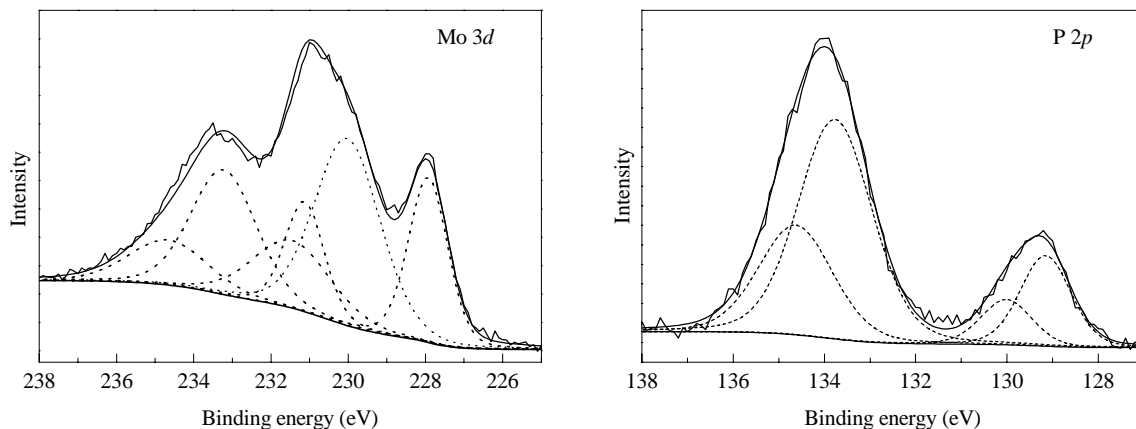


图 2 MoP 催化剂的 XPS 谱

Fig. 2. XPS spectra of the MoP catalyst.

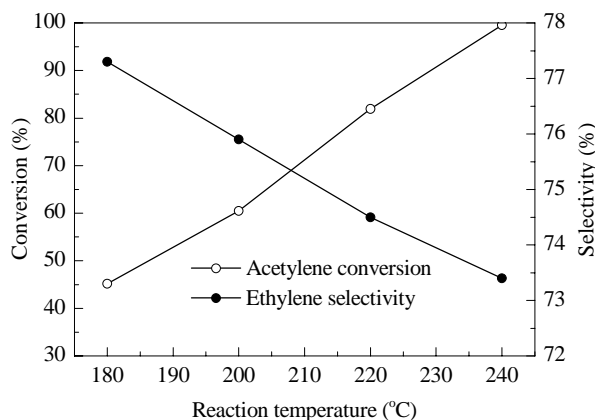


图3 反应温度对加氢活性的影响

Fig. 3. Influence of reaction temperature on the hydrogenation activity of the MoP catalyst. Reaction conditions: atmosphere, $H_2/C_2H_2 = 10$, $SV = 36000 \text{ ml}/(\text{g}\cdot\text{h})$.

XRD 和 XPS 结果表明, 钼磷酸盐前驱体在 650°C 可被 H_2 还原形成 MoP 物相. MoP 催化剂的红外光谱结果表明, 在 $2040\sim 2060 \text{ cm}^{-1}$ 处形成了吸附于 Mo 原子上的线式吸附态 CO 的红外吸收带, 这与 Pt, Pd 和 Rh 等贵金属上 CO 的吸附相似^[12]. 由此推知, MoP 具有与贵金属相似的性能, 能很好地活化 H_2 分子形成活性氢物种. 因此, MoP 催化剂表现出与贵金属相似的催化乙炔加氢活性.

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英 译 文

English Text

The ethylene obtained from thermal cracking and steam cracking contains small quantities of acetylene ($< 2\%$), which poisons ethylene polymerization catalysts. The selective hydrogenation of acetylene has been extensively investigated over Pd and promoted Pd catalysts. However, since the hydrogenation of acetylene is a series reaction ($C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$), the selectivity for ethylene decreases drastically with increasing acetylene conversion [1–3]. Unpromoted Pd catalysts have high activity for trace acetylene elimination, while they suffer from low ethylene selectivity at high acetylene conversions. Although most selective hydrogenation of acetylene studies to date have involved Pd-based systems, other catalysts have also been considered [4–6]. However, these studies focused on precious metal catalysts rather than a non-noble metal catalyst. Molybdenum phosphide (MoP) is a new hydrogenation catalyst that has attracted the attention of researchers. Many studies have shown that the MoP catalyst has superior catalytic activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [7–9] but few studies have paid any attention to their reactivity in other hydrogenation reactions such as acetylene selective catalytic hydrogenation.

In this work, MoP was prepared and used for the selective hydrogenation of acetylene. Ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was mixed with diammonium hydrogen phosphate $(NH_4)_2HPO_4$ in distilled water at a Mo/P molar ratio of 1.0. After the evaporation of water and calcination in air at 500°C for 4 h, the obtained solid was ground to a powder and sieved to 20–40 mesh particles. The obtained particles were placed in a quartz reactor and reduced in a temperature controlled manner from room temperature to 300°C in 30 min and from 300 to 650°C over 175 min at a rate of $2^\circ\text{C}/\text{min}$ in flowing H_2 ($\sim 100 \text{ ml}/\text{min}$). The final temperature was maintained for 2 h followed by cooling to room temperature in H_2 . The sample was then passivated at room temperature for 6–8 h in a stream of $1\%O_2\text{-}99\%N_2$.

The X-ray diffraction (XRD) pattern was obtained using a Rigaku D/Max-2500/PC X-ray diffractometer with $Cu K_\alpha$ radiation. In-situ X-ray photoelectron spectroscopy (XPS) analysis was performed using a KRATOS X-ray source (model VG ESCALAB MK2) with $Al K_\alpha$ radiation. The chemical state of Mo and P in the MoP catalyst was acquired by XPS analysis.

The hydrogenation of acetylene was evaluated in a continuous flow quartz reactor at ambient pressure. 100 mg of catalyst was pretreated at 600°C in a $90 \text{ ml}/\text{min}$ flow of hydrogen for 60 min followed by cooling in H_2 flow to the

desired reaction temperature. The feedstock containing 1 vol% acetylene and 10 vol% hydrogen was balanced with Ar at total flow rate of 60 ml/min and this was controlled by mass flowmeters. The reactants and products were analyzed using an on-line gas chromatograph (Agilent 6890N) equipped with a FID and a GS-GASPRO column (30 m × 0.320 mm).

The crystal structure of the MoP catalyst prepared in hydrogen at 650 °C for 2 h was examined using XRD and shown in Fig. 1. This figure shows a series of typical peaks at $2\theta = 27.94^\circ, 32.08^\circ, 43.06^\circ, 57.16^\circ, 57.74^\circ, 64.78^\circ, 67.06^\circ, 67.58^\circ, \text{ and } 74.12^\circ$, which can be attributed to the (001), (100), (101), (110), (111), (102), and (201) crystal planes of the MoP phase, respectively. Besides the MoP crystal no other new compounds were detected. The results indicate that the perfect MoP crystal was produced by the reduction of molybdenum phosphate in hydrogen at 650 °C.

Figure 2 shows in-situ XPS spectra of the MoP catalyst pretreated at 500 °C for 60 min in pure hydrogen. The Mo $3d_{5/2}$ peak positions for the catalyst is located at electron binding energies of about 228.0, 229.1, and 232.2 eV, and these are with the same as those of Mo^{3+} , $\text{Mo}^{\delta+}$, and Mo^{6+} in a multiphase environment. These results are in agreement with previously reported results [10]. Additionally, the P $2p_{3/2}$ peaks were at 129.2 and 133.4 eV, which is with the same as that for the P^{3-} and P^{5+} species, and this is also in agreement with a previous report [11].

The P^{3-}/P and Mo^{3+}/Mo ratios are 0.22 and 0.24, respectively, on the surface of the MoP catalyst and this is based on

XPS peak areas. The results show that the Mo^{3+} and P^{3-} species (MoP) can be formed by hydrogen reduction. However, some high valence state molybdenum and phosphorus compounds still exist in the MoP catalyst.

The catalytic hydrogenation reaction was investigated at $\text{H}_2/\text{C}_2\text{H}_2 = 10$, a space velocity of 36000 ml/(g·h), and different reaction temperatures for the prepared MoP catalyst. The results are shown in Fig. 3. As shown in Fig. 3, the MoP catalyst has good catalytic hydrogenation activity toward acetylene and the conversion reaches 45.2% at 180 °C. The main hydrogenation product is ethylene and the selectivity exceeds 77.3%. Acetylene conversion and ethylene selectivity is 99.5% and 73.4% at a reaction temperature of 240 °C, respectively.

XRD and XPS results indicated that the molybdenum phosphate precursor material can be reduced by hydrogen to form the MoP phase at 650 °C over 2 h. The characteristic IR band is attributed to linearly adsorbed CO on the Mo atoms of the MoP surface and is similar to the IR bands at 2040–2060 cm^{-1} , which corresponds to CO adsorbed on noble metals such as platinum, palladium, and rhodium [12]. The results imply that MoP has good catalytic hydrogenation performance similar to noble metals and that it is the main active centre for the hydrogenation reaction. Therefore, the MoP catalyst showed good activity toward acetylene hydrogenation.

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